The Thermal Isomerization and Nuclear Magnetic Resonance Spectra of Tropyltropolones

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Nozoe et al.[1] have obtained five different tropyltropolones by the reaction of tropylium ions with tropolone. Of those tropyltropolones, structures for isomeric 5-tropyltropolone (II) and 3-tropyltropolone (III) have been suggested on the basis of ultraviolet spectral data.[1]

In order to obtain a more definite basis for the assigned structures, the present author has compared the nuclear magnetic resonance (NMR) spectra of several tropilidene derivatives and found the assigned structure to be correct. This paper will deal with these results, as well as with the thermal isomerization of tropyltropolones.

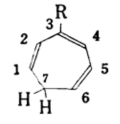
In the 40 Mc. NMR spectra of 5-tropyltropolone (I), a triplet ($J=4.0$ c.p.s.), a quartet, a multiplet and a triplet ($J=1$ c.p.s.) appear at 7.34, 4.82, 3.87 and 3.44 τ respectively. The proton ratio of these absorptions is 1 : 2 : 2 : 2 (Fig. 1). In the NMR spectra of the other 7-substituted tropilidenes (III, IV, V, VI, VII, VIII and XI), the same coupling patterns concerning the absorption of the tropyl group appear at approximately the same position and with the same proton ratio as those of 5-tropyltropolone, as is indicated in Table I. Therefore, the author has classified the proton absorptions of the tropyl group of those derivatives into four groups: A, B, C and D.*

A is a triplet ($J=4\sim6$ c.p.s.) at $6.5\sim7.8\,\tau$ (the position of which is especially affected by the substituent group at C_7), B is a quartet at $4.5\sim4.8\,\tau$, C is a multiplet at $3.6\sim3.9\,\tau$, and D is a triplet ($J=2\sim3$ c.p.s.) at $3.3\sim3.5\,\tau$.

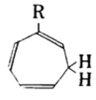
Proton assignments of tropilidene have been made by Burton et al.[2] and by Isobe[3]. A comparison of these results shows that the absorptions A, B, C and D should be assigned to the protons at C_7, C_1+C_6, C_2+C_5 and C_3+C_4 respectively.

Taking this assignment into account, we will compare the NMR spectra of isomeric 5-tropyltropolone (II) with I to derive a reasonable structure for II.

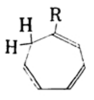
Three possible formulae can be written for the isomeric 5-tropyltropolone structure (IIa, IIb and IIc):



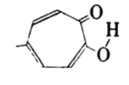
IIa



IIb



IIc

R=


The triplet at 7.71 τ in the NMR spectrum of II rules out the formula IIc. The formula

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[1] T. Nozoe, T. Mukai and T. Tezuka, This Bulletin, **36**, 1470 (1963).

* The 60 Mc. NMR spectra of phenyltropilidene (VII), taken with a Varian Associate HR-60 spectrometer, reveals that the basic coupling pattern is just the same as that of 40 Mc. The only difference is that the former has the fine structure of the each peak, A, B, C and D, due to the long-range coupling. The author wishes to thank Dr. Roy King for his measurement of the NMR spectra and his discussions.

[2] R. Burton, L. Pratt and G. Willikinson, *J. Chem. Soc.*, **1961**, 594.

[3] T. Isobe, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

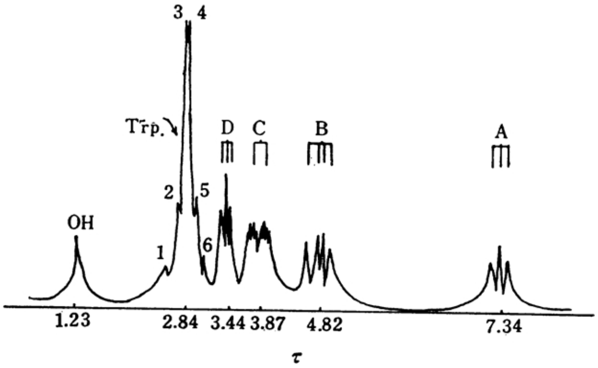


Fig. 1. NMR spectrum of compound I at 40 Mc.

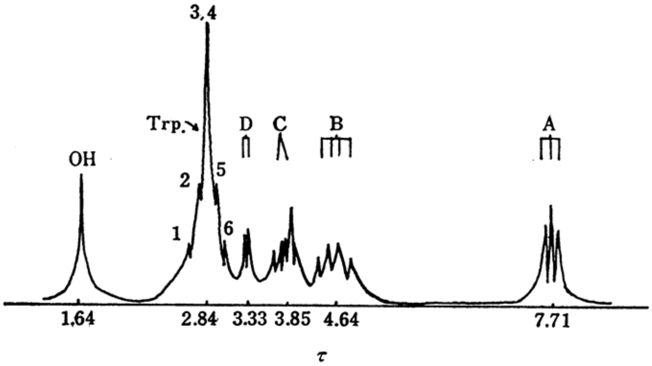


Fig. 2. NMR spectrum of compound II at 40 Mc.

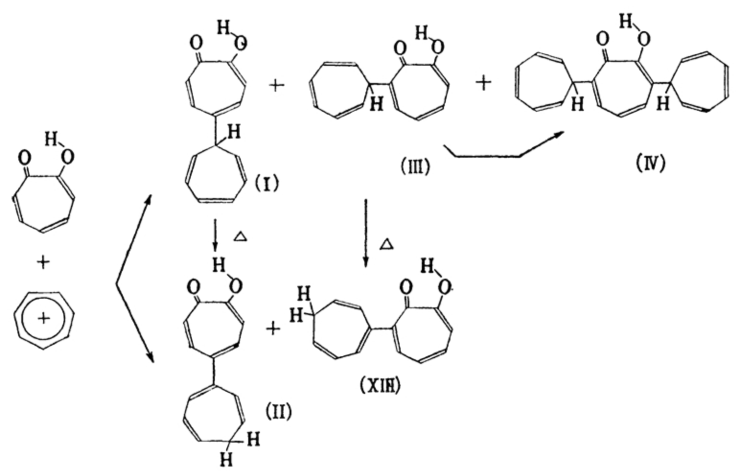
IIb may also be ruled out for the following reasons.

In the NMR spectra of I and II, the most significant difference is observed in the absorptions C and D. In the NMR spectrum of II (Fig. 2) a doublet (J=4.4 c.p.s.) and a multiplet appear at 3.33 τ (corresponding to the D absorption) and at 3.85 τ (C) respectively, while in the NMR spectrum of I a triplet and a multiplet apprear at 3.44 τ (D) and at 3.87 τ (C) respectively. The proton ratio of the absorption D to the absorption C of II is 1 : 2, while that of I is 2 : 2. These results are most reasonably explained by assuming the formula IIa thus ruling out IIb. A proton of C_4 in IIa appears at 3.33 τ, giving rise to a doublet, and the protons of C_2+C_5 at 3.84 τ, giving the multiplet. Therefore, the formula IIa is concluded to be correct for the structure of II; this is quite consistent with Nozoe's result.1)

Nozoe et al.1) have also mentioned that the isomeric 5- and 3-tropyltropolones, II and XIII, were obtained when the raection mixture of tropylium ions and tropolone was distilled at 180°C while the other tropyltropolones, I, III and IV, were obtained when the separation was carried out with the reaction mixture by recrystallization. This evidence seems to suggest that the isomeric tropyltropolones II and XIII come from either I, III, or IV by thermal isomerization when distilled. This assumption is justified as follows. The distillation of 5-tropyltropolone (I) at 180°C gives an oil (b. p. 173°C/3 mmHg) which soon crystallizes to afford the isomeric 5-tropyltropolone (II) (m. p. 98°C) in a good yield. Because only a small amount of 3-tropyltropolone (III) is available, the thermal isomerization reaction has not been carried out with III. The same treatment of 3, 7-ditropyltropolone (IV), however, gives neither the isomeric 3, 7-ditropyltropolone nor 3- and 5-tropyltropolones, XIII and II. Therefore, it may be concluded on the basis of the evidence given by Nozoe et al.1) and by the present author that the isomeric 3-tropyltropolone (XIII) comes from III by thermal isomerization. 3, 7-Ditropyltropolone (IV) is derived from 3-troplytropolone (III) by the reaction of one mole equivalent of tropylium ions.

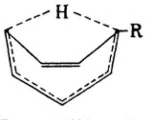
The above relationship between tropyltropolones can be given as:

The isomer IIa was the only product obtained by the isomerization of I. The reason for this is that the most stable isomer with regard to the length of the conjugated system



and the steric conditions is IIa. While IIc has the longest conjugation system between three double bonds of the tropyl group and the tropolone molecule, the methylene group of C_7 prevents the coplanality of the tropyl group with the tropolone molecule, thus inhibiting the resonance stabilization, and making IIc less stable than IIa. In IIb, there is no such steric hindrance, but the conjugated system is shorter; thus IIb is less stable than IIa.

For the mechanism of the migration of hydrogen in the thermal isomerization of 7-d-tropilidene, Ter Borg et al.[4] have proposed the 1, 5-transannular migration of hydrogen, as is pictured in XIV. It is also probable that the 1, 5-transannular migration of hydrogen is involved in our case, as is indicated in XV.[5] The conjugation of the tropolone molecule in the transition state decreases the activation energy for this migration, facilitating the isomerization.



XIV : R=D XV : R=Tropolone

The auther wishes now to discuss the NMR spectra of the tropilidene derivatives listed in Table I.

The most striking fact to be pointed out is the difference in the chemical shift of the methine and methylene protons (absorption A) of those derivatives. Looking at the chemical shift of methine protons of the compounds I, VII and VIII, we find that these protons appears at a lower field by 0.4∼0.5 p.p.m. than the methylene protons of tropilidene (XII). On the other hand, the methylene protons of the tropyl derivatives, II, IX and 3-phenyltropilidene,[11] which are the isomer of I, VIII and VII respectively, appear at approximately the same position as tropilidene (XII). Obviously, the cause of this low field shift of the methine protons should be attributed to the effect of the phenyl or tropolone molecule substituted at the C_7 of tropilidene. However, it is rather surprising that the low field shift is not so large as would be expected from the usual substituent effect of the phenyl group.[6]

α-Protons are usually affected by the phenyl group to show a low field shift of approximately 1.5 p.p.m. when the phenyl group is substituted for hydrogen on an alkane.[6] Thus the methylene protons of *n*-propane appear at 8.75 τ, while the methine proton of isopropylbenzene appears at 7.10 τ.[6]

The reason for this small shift seems to be that the double bonds of the tropyl group have some shielding effect upon the methine proton.[7,8] Although the theory and the magnitude of the shielding effect of the tropyl group are not clear, we can understand such a tendency of the tropyl group when we look at the NMR spectrum of ditropyl (XI). The shift of the methine protons of XI are slightly higher than that of the methylene protons of tropilidene, suggesting that the double bonds of the tropyl group have the effect of increasing the effective shielding of the methine proton at C_7.[7,8]

The fact that the methine proton of 5-tropyltropolone (I) shifts to a low field by the

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4) Ter Borg, H. Kloosteaziel and N. van Meurs, *Proc. Chem. Soc.*, **1962**, 359.

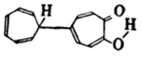
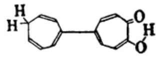
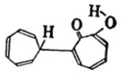
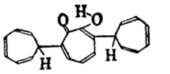
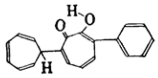
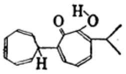
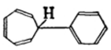
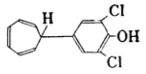
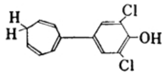
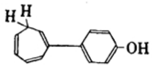
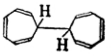
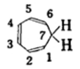
5) The author has found that the compound VIII is also converted to IX upon heating at 200°C. T. Tezuka, unpublished work.

6) L. M. Jackman, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, London (1959), pp. 58-60.

7) The author is deeply indebted to Professor Orville L. Chapman for discussing the shielding effect of the double bonds of the tropyl group.

8) O. L. Chapman, T. Tezuka and R. King, to be published.

TABLE I. THE PROTON CHEMICAL SHIFT OE THE TROPYL GROUP IN THE SUBSTITUTED TROPILIDENES

No.	Compound	Group				
		A (τ)	B	C	D	Ref.
I		7.34 ($J=4.0$)	4.82	3.87	3.44	1 (J=c.p.s.)
II		7.71 ($J=6.0$)	4.64	(3.85)	(3.33)	1
III		6.50 ($J=5.7$)	4.76	3.88	3.52	1
IV		6.48 ($J=5.1$)	4.64	3.76	3.40	1
V		6.37 ($J=4.8$)	4.82	3.87	3.63	10
VI		6.58	4.72	3.80	3.46	10
VII		7.30 ($J=5.0$)	4.78	3.80	3.34	11, 12
VIII		7.41	4.57	3.85	3.33	5
IX		7.67	4.50	3.62	3.28	5
X		7.75 ($J=6.7$)	4.64	—	—	14
XI		8.10 ($J=3.0$)	4.82	3.88	3.42	13
XII		7.84 ($J=6.2$)	4.81	3.94	3.54	2, 3

same degree as in phenyl tropilidene (VII) indicates that the tropolone molecule also has the effect of deshielding the methin protons by the same degree as benzene. Probably, the six-π-electron circulation in the tropolone molecule occurs when it is placed in a magnetic field as in the benzene molecule.

One more point of interest is that the different coupling patterns of the tropolone ring protons are observed with different tropyltropolones. The ring protons of 5-tropyltropolones (I and II) are expected to show A_2B_2-type coupling, while 3, 7-ditropyltropolone (IV) show AB_2-type coupling. Actually, the symmetrical A_2B_2-type coupling[9] are observed at 2.84 τ in the NMR spectra of I and II, as is indicated in Figs. 1 and 2. In the case of I, six lines can be recognized.

An unsymmetrical coupling pattern of the

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[9] L. M. Jackman, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, London (1959), pp. 91-95.

* A figure of the NMR spectra of this compound is indicated in Ref. 10.

[10] T. Nozoe and T. Tezuka, This Bulletin, in press.

[11] T. Nozoe, T. Mukai, T. Tezuka and K. Osaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 662 (1963).

[12] H. Horino obtained phenyltropilidene (VII) as colorless crystal (m. p. 32°C) and kindly provided a sample; to him the authors thanks are due.

[13] Professor Toshio Mukai kindly gave the sample of ditropyl (XI) (m. p. 61°C); the author wishes to thank him.

[14] K. Kitahara, Doctoral Thesis, Tohoku Univ. (1963).

tropolone ring proton of compound IV[1],* is oberved which is very similar to the theoretical pattern of the AB_2 system.[9] Almost the same coupling is observed for the ring protons of compound VI.[10],*

The methine proton lines of the tropyl group of compounds III, IV, V and VI, in which the tropyl groups are present at the ortho-position of tropolone, appear at an even lower field than those of compounds I, VII and VIII. The chemical shifts of those protons are lower by 1.3 p.p.m. than the methylene protons of tropilidene. The methine protons of III, IV, V and VI will be greatly deshielded by both the ring current and the oxygen functions of of tropolone. However, the details of these effects are too complicated to discuss here; further studies are necessary.

Experimental

Isomeric 5-Tropyltropolone (II) from I. — I (500 mg.) was heated at 180~200°C for 20 min. and then distilled to give an oil, b. p. 170°C/4 mmHg, which soon crystallized to afford 500 mg. of crystals, m. p. 80~85°C. Recrystallization from the mixed solvent of ethanol and benzene gave yellow needles, m. p. 98°C (II), identified by a mixed melting point determination and by a comparison of the infrared spectra with those of an authentic sample.[1]

3, 7-Ditropyltropolone (IV) from III.—A mixture of 250 mg. of III and 117 mg. of ditropylether[14] in 2.5 ml. of absolute ethanol was heated under reflux for 3 hr. The evaporation of the solvent gave 360 mg. of crystals, m. p. 90~100°C, which afforded yellow needles, m. p. 135°C (IV), on recrystallization from ethanol. The crystals obtained were confirmed to be identical with 3, 7-ditropyltropolone[1] by mixed melting point determination and by a comparison of infrared spectra.

NMR Spectra Measurement.—The NMR spectra of the tropyl derivatives (I—X) were measured with a Varian Associates V 4200 B spectrometer (40 Mc.) in carbon tetrachloride solutions, using cyclohexane as an inner reference.* The NMR spectrum of IX was measured with a 60 Mc. Hitachi NMR spectrometer in a carbon tetrachloride solution, using tetramethyl silane as an inner reference.

The author wishes to express his gratitude to Professor Tetsuo Nozoe for his guidance throughout this study. The author also wishes to express many thanks to Professors Toshio Mukai, Kahei Takase, Taro Isobe, Dr. Takashi Toda and Mr. Kenichi Abe for their helpful discussions and assistance.

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* For the NMR measurement, the author wishes to thank Mr. Kensuke Takahashi, Dr. Masaki Iwaizumi and Mr. Makoto Hanabuchi.